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Nitrogen dioxide gas sensing using reduced graphene oxide-copper oxide multilayer structure

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Abstract:

Reduced graphene oxide and copper oxide hybrid structures were fabricated in two ways: as a composite mixed structure and in a multilayer configuration. The RGO/CuO multilayer exhibited the best sensitivity in response to the oxidizing NO_2 atmosphere. The model explaining observed properties of the sensing structure was introduced and shortly discussed.

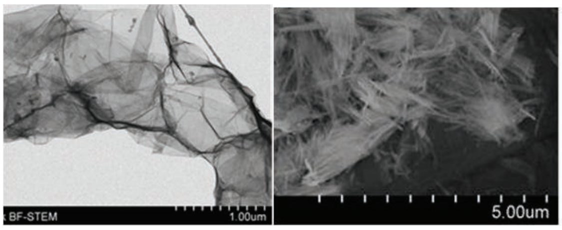
Key words: graphene gas sensor, graphene oxide, reduced graphene oxide, rGO/metal oxide nanostructure.

Introduction

Graphene materials in a form of both the pristine graphene (PG) and modified graphene materials as graphene oxide (GO) and reduced graphene oxide (rGO) are used in gas sensor applications [1]. GO and rGO are cheap in production, offering easy large scale manufacturing. These materials exhibit high carrier mobility at room temperature and due to 2D structure have a large surface area. The most important property of graphene based materials enhancing their gas sensitive properties is however the intensive adsorption of ambient gas molecules influencing the electronic transport. Heavily oxidized GO is not electrically conductive. It can be transformed to rGO by e.g. appropriate temperature annealing [2]. The obtained partially reduced rGO is a material with many functional groups and defects which can interact with the ambient atmosphere. Recent investigations indicate that metal oxide/rGO hybrids can be obtained with improved sensitivity to various gas species [3].

Technology of samples

Graphene oxide was prepared using modified Hummers method [4]. Graphite powder was treated with concentrated sulphuric acid, sodium nitrate and potassium permanganate at temperature around 10ºC. After 60 min. the temperature was raised up to 30ºC and was maintained under stirring for 2 hrs. Next, the distilled water was added to the mixture and temperature was raised up to 100ºC. After 60 min. a small amount of hydrogen peroxide was added. To purify the GO water suspension the GO water slurry was filtrated and then rinsed with distilled water till pH of the filtrate attained 6.0. Obtained single GO flakes reached up to 6 nanometers in thickness with 10 micrometers in a lateral size (Fig. 1a).



(a) (b)

Fig. 1. TEM image of GO flakes (a) and SEM image of CuO nanoparticles (b).

Cupric oxide CuO was obtained as follows: to 100 ml of 0.1 M solution of $CuSO_4$ at 100 °C, 500 ml of 0.1 M NaOH solution was added. The resulting black suspension was heated for 30 min. at this temperature. The precipitate was washed with hot water on a polyethersulphone filter with pore size of 0.2 µm. Obtained layer in a form of CuO nanoparticles, Fig.1(b), behaved as p-type material (metal vacancies result in the production of holes).

The CuO-GO composite was obtained by mixing of 25 ml 0.01% CuO aqueous suspension with 25 ml 0.01% GO aqueous suspension. The mixture was dispersed using the Hielsher UP 400S ultrasonic disintegrator for 30 min.

One kind of prepared samples was CuO-GO composite which was deposited by spray coating. The thickness of the composite was ca 20 nm. The second kind of structure was a multilayer consisting of GO and CuO thin layers deposited on the substrate by the spray LbL (layer by layer) coating technique. CuO was always the top layer. In total, the sandwich structure consisted of 3 GO and 3 CuO layers.

Gas response of investigated structures

All structures used in investigations were previously annealed in air at 200^{o}C. The values of resistance of single CuO sample and CuO/rGO composite were in the GZ range at room temperature. Single rGO layer was sensitive to NO_2 gas at RT, but its resistance was in the tens of Mohm range. The best sensitivity at RT revealed multilayer CuO/rGO structures, Fig 2.

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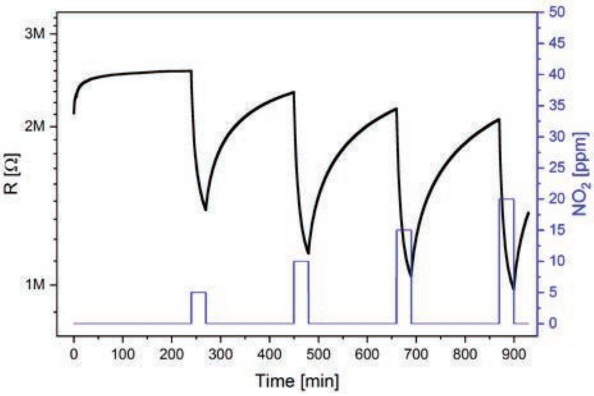

Fig.2. Variation of rGO/CuO multilayer resistance (3x3 layers) after interaction with changed NO_2 concentration.

In explaining the mechanism of interaction of layer by layer rGO/CuO structure with the ambient NO_2 atmosphere the authors envisaged additional influence of the junctions formed in this LbL structure, Fig.3.

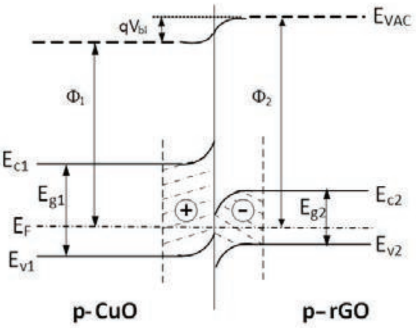

Fig. 3. Formation of an isotype p-CuO/p-rGO heterojunction with hole accumulation layer on the CuO side and hole depletion layer on the rGO side. Φ is the work function for a given semiconductor.

For the isotype p-CuO/p-rGO heterojunction due to the difference in work functions, during junction formation electrons transfer from CuO to rGO and holes transfer in the opposite direction. In effect a depletion layer is formed on the rGO side and accumulation layer on the CuO side. When the junction is exposed to the oxidizing NO_2 gas atmosphere, electrons transfer from rGO and CuO to adsorbed NO_2 leading to the increase in the hole concentration in both materials. This additionally causes further increase of carriers concentration in the accumulation layer on CuO side, what gives additional decrease of the sensor resistance. The effect of conductivity enhancement can be explained by the analysis of measurement configuration of the multilayer sample, Fig.4.

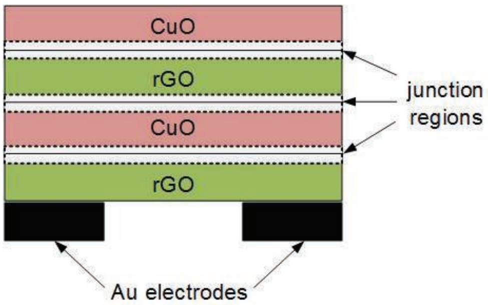

Fig. 4. Measurement configuration of the multilayer rGO/CuO structure. The regions of heterojunctions influence additionally the sample conductance.

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